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PHOTOELECTRON ANGULAR DISTRIBUTIONS FROM H_2 and D_2

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ABSTRACT

The photoelectron asymmetry parameters of H_2 and D_2 were measured using synchrotron radiation over the 19–27 eV photon energy range. The results are compared with previous measurements and several theoretical calculations. A few of the theoretical calculations are in good agreement with experiment, but most of them predict asymmetries which are too large. Essentially identical β values were measured for H_2 and D_2 . This result is discussed in terms of differences which could arise due to vibrational and rotational structure.

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INTRODUCTION

The relatively simple two-electron structure of H_2 has made it a prototype system for study in the development of theoretical models of molecular photoionization. The photoionization process is described by

Angular momentum and parity conservation restrict the form of the photoelectron angular distribution [1]. Photoejection from randomly oriented target molecules by electric dipole interaction with a linearly polarized photon beam is described by a differential cross section of the form

$$\frac{d\sigma(\epsilon)}{d\Omega} = \frac{\sigma(\epsilon)}{4\pi} [1 + \beta(\epsilon) P_2(\cos\theta)] \quad (2)$$

Here $\sigma(\epsilon)$ is the angle-integrated cross section, $P_2(\cos\theta) = \frac{1}{2} (3 \cos^2\theta - 1)$, θ is the photoelectron ejection angle with respect to the polarization vector of the photon beam, ϵ is the photoelectron kinetic energy, and $\beta(\epsilon)$ is the asymmetry parameter. $\beta(\epsilon)$ completely characterizes the angular distribution. It is restricted to values in the range $-1 \leq \beta(\epsilon) \leq 2$.

In the united-atom limit of photoemission for molecular hydrogen, namely $He\ 1s \rightarrow \epsilon p$, an energy-independent asymmetry $\beta = 2$ is required [2], so that deviations from $\beta = 2$ reflect the non-spherical molecular

structure of H_2 . This result illustrates the general motivation for the measurement and theoretical calculation of molecular photoelectron asymmetries, i.e., $\beta(\epsilon)$ is sensitive to the anisotropic, molecular electronic structure [3]. Thus, $\beta(\epsilon)$ for the photoionization of H_2 is determined by the dipole matrix elements and relative phases for the two continuum channels $1\sigma_g \rightarrow \epsilon\sigma_u$ and $\epsilon\pi_u$ (see, for example, Dill [5]). Several theoretical calculations of $\beta(H_2)$ have been published [4-17], and a number of groups have measured $\beta(H_2)$ using discrete resonance line radiation [18-24]. Recently, Marr et al. [25] reported measurements over the photon energy range 18-30 eV using synchrotron radiation.

There is rough agreement among the theoretical values of $\beta(H_2)$, with a range of 0.2-0.3 β unit, and among the experimental values, with a similar range. However, detailed agreement is absent. In particular, the β values of Marr et al. [25] are consistently lower than those measured using resonance lamps. In light of these residual discrepancies, and because we have an apparatus that is relatively free of the systematic errors usually inherent in β measurements, we have made another synchrotron radiation based set of $\beta(H_2)$ measurements, reported below. Also included are results for D_2 , which comprise another motivation for this work.

EXPERIMENTAL

The apparatus has been described previously [26], and the experimental method and data analysis procedures have been discussed in detail in a concurrent publication [27]. Hence, a brief description is given here. The time structure of the synchrotron radiation at the Stanford Synchrotron Radiation Laboratory was used to record time-of-flight (TOF) photoelectron spectra. Two TOF detectors were operated simultaneously, one positioned at 0° and the other at 54.7° with respect to the polarization vector of the photon beam. Equation (2) shows that $\beta(\epsilon)$ is determined by the relative intensities of photoelectrons ejected at two angles. The apparatus was calibrated for angular distribution measurements by recording photoelectron lines of the rare gases at photon energies where the $\beta(\epsilon)$ values have been accurately measured [28]. This double-angle-TOF technique offers certain major advantages for the measurement of electron asymmetries. Because all of the ejected electrons, at both angles, are recorded simultaneously, the collection efficiency (or signal/noise ratio) is greatly enhanced. Also, in contrast with the usual technique of a single rotatable detector, we eliminate the need to correct the photoelectron intensities for variations in the sample gas density and photon beam intensity, thus reducing systematic error.

RESULTS AND DISCUSSION

In Table 1 are listed our measured values of $\beta(\text{H}_2)$ and $\beta(\text{D}_2)$, representing the total photoelectron bands, i.e., summed over all rotational and vibrational transitions. These results are plotted in Fig. 1 along with theoretical curves, the measurements of Marr et al. [25], and the resonance line measurements of Morgenstern et al. [20]. All of the theoretical calculations predict a large asymmetry and a slow variation of $\beta(\text{H}_2)$ with energy, but they differ in the precise magnitude of $\beta(\text{H}_2)$ and the slope of the energy variation. The present measurements agree well with the earliest published theoretical calculations: those of Tully et al. [4], of Shaw and Berry [6], and with the semi-empirical threshold value calculated by Dill [5]. A least-squares line fit through the present measurements of $\beta(\text{H}_2)$ and $\beta(\text{D}_2)$ indicates that β slowly increases with increasing energy.

Accurate measurements of $\beta(\text{H}_2)$ are clearly required for a critical evaluation of the theoretical calculations. The resonance line measurements [18-24] tend toward larger asymmetries than has been measured using synchrotron radiation. We note that the resonance line radiation is concentrated into a much smaller bandpass ($\Delta h\nu \approx 10$ meV FWHM), than the synchrotron radiation ($\Delta h\nu \approx 100$ meV FWHM). Hence, photoelectron measurements using the two radiation sources greatly differ in their sensitivity to any possible resonance or threshold structure in the photoabsorption spectrum. In particular, the Ne(I) resonance lines at $h\nu = 16.85$ eV and 16.67 eV, with which the largest measured asymmetries plotted in Fig. 1 were obtained, lie energetically

between vibrational thresholds of H_2^+ . A recent theoretical study [17] of vibrational preionization in H_2 would indicate that the Ne(I) line β measurements are almost certainly influenced by autoionization. The measurements reported here were obtained over a photon energy range where only direct ionization apparently occurs [37]. At $h\nu \approx 27$ eV, however, Dehmer et al. [29] have detected weak structure attributed to a doubly-excited state of H_2 .

We should comment also on the analysis of Kibel et al. [23] concerning loss of observed asymmetry due to elastic scattering of the photoelectrons before they reach the detector. In the present technique elastic scattering is accounted for, to a great extent, by the calibration procedure (see the discussion in Ref. [27]). Even if scattering decreases the experimental photoelectron asymmetry, the observed asymmetries are scaled to the known β values of the calibration lines. The calibration procedure amounts to an "adjustment" of the experimental asymmetries to account for elastic scattering (and other experimental non-idealities [27]) in the spirit of the adjustments adopted by Kibel et al. In particular, we believe the present results are not too low, because we also obtain an observed " β value" of 2.06 ± 0.03 as an average for the He 1s $\rightarrow$ ϵp asymmetry over $h\nu = 27-32$ eV; i.e., a value that is slightly too high, because values over 2 are not possible.

Virtually identical β values were observed for H_2 and D_2 , within the precision of the measurements. The averages of the measurements listed in Table 1 give $\beta(H_2) = 1.71 \pm 0.02$ and $\beta(D_2) = 1.73 \pm 0.02$ over $h\nu = 19\text{--}27$ eV. It is of interest to inquire whether different β values should be expected for H_2 and D_2 , and to determine which factors might produce a variation. If the Born-Oppenheimer separation of nuclear and electronic wavefunctions is adopted for a diatomic molecule, the electronic states are characterized by potential curves [30], which represent the sum of electronic energy plus nuclear Coulombic repulsion as a function of internuclear distance. Other than a very small difference due to variations in the reduced mass, the potential curves are independent of nuclear mass, so identical curves represent the $X^1\Sigma_g^+$ and $X^2\Sigma_g^+$ states of H_2 and D_2 and of H_2^+ and D_2^+ , respectively. Nearly identical wavefunctions therefore describe the motion of the photoelectron in the (fixed-nuclei) field of the molecular ion. The β measurements reported here, in which rotational and vibrational structure was not resolved, essentially represent the vertical overlap of the $X^1\Sigma_g^+$ and $X^2\Sigma_g^+$ potential curves. Since these are identical for the two isotopes, identical β values are expected.

The reduced mass of D_2 is twice that of H_2 . Thus, when the fixed-nuclei approximation is lifted, quite different energies result for the rotational and vibrational levels. Considering first the vibrational structure, Itikawa [14,31] has shown theoretically that the photoionization transition moment varies significantly with the

internuclear separation. This effect, along with a dependence of the transition moment on photoelectron energy, leads to non-Franck-Condon vibrational branching ratios and β values which vary appreciably with the vibrational level of the ionic state. These effects have been confirmed by Berkowitz and Spohr [32] in measurements of vibrational branching ratios for H_2^+ , D_2^+ , and HD^+ , and later for H_2^+ by Gardner and Samson [33]. Kreile and Schweig [24] have recently measured β values at 21.22 eV for vibrational levels of H_2^+ which vary in excellent agreement with theory [14]. Thus, for the vibrationally averaged results of the present experiment, we would expect a difference between $\beta(\text{H}_2)$ and $\beta(\text{D}_2)$ to the extent that the transition moment is weighted differently over the internuclear separation and photoelectron energy. The vibrationally resolved photoelectron spectra of H_2 and D_2 differ qualitatively in the vibrational branching ratios [32], but this is due primarily to the quite different energy spacing of the vibrational levels in the ionic state. The centers of gravity of the photoelectron bands occur at nearly the same binding energy, which is consistent with the model of a vertical transition between the ground and ionic potential curves. Therefore, considering that the variation of $\beta(\text{H}_2)$ with vibrational level is rather small [24], only a small difference between $\beta(\text{H}_2)$ and $\beta(\text{D}_2)$ is expected for the vibrationally averaged photoelectron bands, in good agreement with experiment.

A strong variation between $\beta(\text{H}_2)$ and $\beta(\text{D}_2)$ would be expected if a significant difference were to occur in the rotational structure

of the photoelectron spectra. Dill [5] has used the angular momentum transfer formalism to show that strong variations in $\beta(\text{H}_2)$ are expected among particular $N \rightarrow N'$ rotational transitions. Rotational structure has been partially resolved in photoelectron spectra of H_2 using resonance line radiation [21,34,35]. About 90 percent of the transitions occur with $\Delta N = 0$, i.e., with no change in the rotational quantum number. The remaining 10 percent of the transition probability occurs with $\Delta N = \pm 2$. Dill [5] has shown that the $\Delta N = 0$ transitions proceed predominantly with zero angular momentum transferred to molecular rotation, with the result that $\beta(\Delta N = 0) \approx 2$. In contrast, the $\Delta N = \pm 2$ transitions occur with the transfer of two units of angular momentum and have much smaller asymmetries. To good approximation, the photoelectron is produced only in p-waves ($\ell = 1$), and in this limit, $\beta(\Delta N = \pm 2) = 0.20$. The calculations of Itikawa [14] for $\beta(\text{H}_2)$, which include the effects of higher partial waves, also predict this strong qualitative difference between $\Delta N = 0$ and $\Delta N = \pm 2$ photoelectron asymmetries. The rotationally resolved measurements of Niehaus and Ruf [21] indeed found $\beta(\Delta N = 0) \approx 2$, with a much smaller asymmetry observed for $\Delta N = 2$. Thus, if an appreciable difference should occur between H_2 and D_2 in the relative weights of $\Delta N = 0$ and $\Delta N = \pm 2$ transitions, a strong variation between $\beta(\text{H}_2)$ and $\beta(\text{D}_2)$ would result for the rotationally averaged photoelectron bands.

A variation between H_2 and D_2 in the rotational structure of their photoelectron spectra might occur due to the vibration-rotation interaction [36] or due to the coupling of electronic and nuclear

motions. Itikawa [14] has computed transition strengths and asymmetry parameters for specific ro-vibrational transitions in the photoelectron spectrum of H_2 . Coupling between electronic and nuclear motions was neglected as well as vibration-rotation interaction. However, the predicted relative intensities of the ro-vibrational transitions are in good agreement with the measurements of Morioka et al. [35] at 21.22 eV. In particular, the theory accurately predicts the variation with final vibrational level of the relative intensity of $\Delta N = 2$ transitions. This indicates that electronic-nuclear and rotation-vibration interactions do not appreciably modify the rotational structure. In the absence of these effects, the rotationally averaged $\beta(H_2)$ and $\beta(D_2)$ are the same, as observed here experimentally.

It is important to clarify a point raised by Marr et al. [25] concerning theoretical calculations of $\beta(H_2)$. Those authors suggest that the discrepancy between their measurements and the much higher asymmetries predicted by fixed-nuclei calculations [9,11] is due to neglect of the $\Delta N = 2$ transitions in the calculations. This appeared to be a reasonable interpretation, since Dill [5] calculated a rotationally averaged $\beta(H_2) = 1.71$, which is in better agreement with the previous [25] and present synchrotron radiation measurements. However, as described by Dill [5], his expression for the rotationally averaged $\beta(H_2)$ is entirely equivalent to the fixed-nuclei type of calculation [4], where rotational transitions are not explicitly considered. In the calculations of $\beta(H_2)$ reported to date [5,12-15] in which values for specific rotational transitions are obtained, the

transition dipole matrix elements and continuum wave phase shifts do not depend on the rotational quantum numbers. The dependence of the differential cross section on the quantum numbers N and N' appears through the squares of angular momentum coupling coefficients, which serve as weighting factors for rotationally-independent transition probabilities [5,38]. When summed over the final rotational level N' , however, the weighting factors sum to unity and the $\beta(H_2)$ expression is independent of N and N' . The $\Delta N = \pm 2$ transitions, as well as $\Delta N = 0$, are implicitly included in the fixed-nuclei calculations. The theoretical curves plotted in Fig. 1 differ only in the accuracy with which the dipole matrix elements and continuum wave phases are calculated. The rotationally averaged calculations of Refs. 12-15 all predict $\beta(H_2)$ curves higher than was measured, while the fixed-nuclei calculations of Refs. 4 and 6 agree well with experiment. The $\beta(H_2)$ values will, however, depend on rotational quantum numbers if the vibration-rotation or electronic-nuclear interactions are included.

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REFERENCES

1. C. N. Yang, Phys. Rev. 74 (1948) 764; M. Peshkin, Adv. Chem. Phys. 18 (1970) 1; V. L. Jacobs, J. Phys. B: Atom. Molec. Phys. 5 (1972) 2257; K.-N. Huang, Phys. Rev. A 22 (1980) 223.
2. J. Cooper and R. N. Zare, in Lectures in Theoretical Physics, S. Geltman, K. Mahanthappa, and W. Brittin, eds., Gordon and Breach, New York, 1969, Vol. 11C, p. 317; W. R. Johnson and C. D. Lin, J. Phys. B: Atom. Molec. Phys. 10 (1977) L331.
3. See, for example, D. Dill and J. L. Dehmer, J. Chem. Phys. 61 (1974) 692; Phys. Rev. Lett. 35 (1975) 213; J. Chem. Phys. 65 (1976) 5327; S. D. Druger, J. Chem. Phys. 64 (1976) 987.
4. J. C. Tully, R. S. Berry, and B. J. Dalton, Phys. Rev. 176 (1968) 95.
5. D. Dill, Phys. Rev. A 6 (1972) 160.
6. G. B. Shaw and R. S. Berry, J. Chem. Phys. 56, (1972) 5808.
7. J. J. Huang and F. O. Ellison, Chem. Phys. Lett. 29 (1974) 565.
8. B. Ritchie, J. Chem. Phys. 63 (1975) 1351.
9. F. Hirota, J. Electron Spectrosc. Relat. Phenom. 9 (1976) 149.
10. O. F. Kalman, Molec. Phys. 34 (1977) 397.
11. C. M. Dutta, F. M. Chapman, Jr., and E. F. Hayes, J. Chem. Phys. 67 (1977) 1904.
12. N. Chandra, Abstracts of Papers of the Xth International Conference on the Physics of Electronic and Atomic Collisions, Commissariat A L'Energie Atomique, Paris, 1977, p. 1210.
13. B. Ritchie and B. R. Tambe, J. Chem. Phys. 68 (1978) 755.

14. Y. Itikawa, Chem. Phys. 28 (1978) 461; 30 (1978) 109; 37 (1979) 401; Chem. Phys. Lett. 62 (1979) 261.
15. L.-Y. Chow Chiu and S. R. Samanta, J. Quant. Spectrosc. Radiat. Transfer 25 (1981) 253.
16. W. Thiel, Chem. Phys. 57 (1981) 227.
17. M. Raoult and Ch. Jungen, J. Chem. Phys. 74 (1981) 3388.
18. J. W. McGowan, D. A. Vroom, and A. R. Comeaux, J. Chem. Phys. 51 (1969) 5626.
19. T. A. Carlson and A. E. Jonas, J. Chem. Phys. 55 (1971) 4913.
20. R. Morgenstern, A. Niehaus, and M. W. Ruf, Abstracts of Papers of the VIIth International Conference on the Physics of Electronic and Atomic Collisions, North-Holland, Amsterdam, 1971, p. 167.
21. A. Niehaus and M. W. Ruf, Chem. Phys. Lett. 11 (1971) 55; a re-analysis of the data of Niehaus and Ruf has been given by E. S. Chang, J. Phys. B: Atom. Molec. Phys. 11 (1978) L69.
22. S. Katsumata, Y. Achiba, and K. Kimura, Chem. Phys. Lett. 63 (1979) 281.
23. M. H. Kibel, F. J. Leng, and G. L. Nyberg, J. Electron Spectrosc. Relat. Phenom. 15 (1979) 281.
24. J. Kreile and A. Schweig, J. Electron Spectrosc. Relat. Phenom. 20 (1980) 191.
25. G. V. Marr, R. M. Holmes, and K. Codling, J. Phys. B: Atom. Molec. Phys. 13 (1980) 283.

26. M. G. White, R. A. Rosenberg, G. Gabor, E. D. Poliakoff, G. Thornton, S. H. Southworth, and D. A. Shirley, Rev. Sci. Instrum. 50 (1979) 1268.
27. S. Southworth, C. M. Truesdale, P. H. Kobrin, D. W. Lindle, W. D. Brewer, and D. A. Shirley, J. Chem. Phys., to be submitted (1981).
28. J. L. Dehmer, W. A. Chupka, J. Berkowitz, and W. T. Jivory, Phys. Rev. A 12 (1975) 1966; A. Niehaus and M. W. Ruf, Z. Phys. 252 (1972) 84; W. H. Hancock and J. A. R. Samson, J. Electron Spectrosc. Relat. Phenom. 9 (1976) 211; J. Kreile and A. Schweig, J. Electron Spectrosc. Relat. Phenom. 20 (1980) 191.
29. J. L. Dehmer, A. C. Parr, J. B. West, K. Codling, and R. Stockbauer, to be published (1981).
30. G. Herzberg, Spectra of Diatomic Molecules, 2nd ed., Van Nostrand Reinhold, New York, 1950, p. 146.
31. Y. Itikawa, J. Electron Spectrosc. Relat. Phenom. 2 (1973) 125.
32. J. Berkowitz and R. Spohr, J. Electron Spectrosc. Relat. Phenom. 2 (1973) 143.
33. J. L. Gardner and J. A. R. Samson, J. Electron Spectrosc. Relat. Phenom. 8 (1976) 123.
34. L. Åsbrink, Chem. Phys. Lett. 7 (1970) 549.
35. Y. Morioka, S. Hara, and M. Nakamura, Phys. Rev. A 22 (1980) 177.
36. D. Villarejo, J. Chem. Phys. 49 (1968) 2523.
37. L. C. Lee, R. W. Carlson, and D. L. Judge, J. Quant. Spectrosc. Radiat. Transfer 16 (1976) 873.
38. U. Fano and D. Dill, Phys. Rev. A 6 (1972) 185.

Table 1. β values measured for the total (rotationally and vibrationally averaged) photoelectron bands of H_2 and D_2 .

$h\nu(\text{eV})$	H_2	D_2
19.0	1.67(5)	1.69(5)
20.0	1.66(6)	1.72(9)
20.6	1.71(8)	...
21.2	1.75(5)	1.82(5)
21.6	1.72(9)	...
22.0	1.70(7)	1.72(6)
23.0	1.77(6)	1.76(7)
24.0	1.66(9)	1.64(7)
25.0	1.70(6)	1.71(6)
26.0	1.76(9)	...
27.0	...	1.77(8)

FIGURE CAPTION

Fig. 1. Experimental β values for H_2 and D_2 with theoretical calculations for H_2 . All of the experimental and theoretical results shown are for the rotationally and vibrationally averaged photoelectron bands. Experimental: $\circ$, present results for H_2 ; $\bullet$, present results for D_2 ; $\square$, Marr et al. [25] results for H_2 ; $\otimes$, Morgenstern et al. [20] results for H_2 . The dashed line is a least-squares fitted line through the present results for H_2 and D_2 . Theoretical curves: A, Chow Chiu and Samanta [15]; B, Ritchie and Tambe [13]; C, Thiel [16]; D, Dutta et al. [11]; E, Hirota [9]; F, Itikawa [14]; G, Tully et al. [4]; H, Shaw and Berry [6]. Theoretical calculations at one energy: J, Dill [5]; K, Chandra [12].

Figure 1.

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